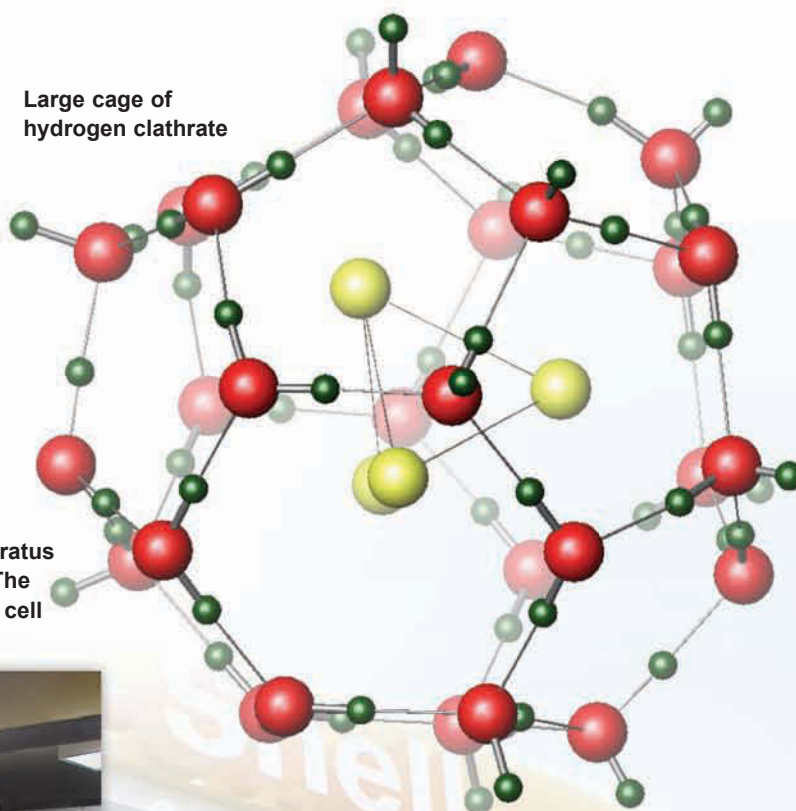**Large cage of hydrogen clathrate**

Konstantin Lokshin works on the apparatus we used to study hydrogen clathrate. The inset is a closeup of the high-pressure cell in which the clathrate formed.

Background photo: (Copyright Shell Hydrogen— www.shell.com/hydrogen)

# Storing Hydrogen in Crystalline Molecular Cages of Water

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Under certain conditions, water mixed with gas will form crystalline cages of water molecules with the gas trapped inside. These "cage compounds"—called clathrate hydrates or simply clathrates—can occur naturally, often under extreme conditions. In fact, methane clathrate, which is found worldwide in ocean floor sediments and permafrost, is believed to contain the largest source of hydrocarbons on Earth. Our studies at the Los Alamos Neutron Science Center show that hydrogen clathrate can trap hydrogen at mass fractions rivaling those of the best materials for hydrogen storage. In addition, we have found a way to capture hydrogen in hydrogen clathrate in as little as a few minutes or less and release it at least as quickly. Neutron diffraction at various pressures and temperatures determined the complete crystal structures of the two types of cages that form in hydrogen clathrate. The results allowed us to revise previous estimates of the numbers and positions of the hydrogen molecules trapped in each type of cage. Our neutron-diffraction studies provide benchmarks for future work on hydrogen clathrate, which could play a significant role in a hydrogen economy.

A t certain pressures and temperatures, a mixture of water and a gas can crystallize into an icy solid known as a clathrate hydrate. Some clathrate hydrates form at pressures up to thousands of atmospheres and/or temperatures less than 0°C; others form at more moderate conditions.

The crystal structures of clathrate hydrates, just like those of common ice, consist of hydrogen-bonded water molecules. However, the water molecules in the clathrate hydrates typically form polyhedral cages in which gas molecules can be physically trapped (see the ball-and-stick models on the opening pages of this article). In fact, a significant fraction of the cages must be filled with guest molecules to stabilize the clathrate structure.

Because clathrate hydrates can store large volumes of gas, they are thought to have played a significant role in the development of the solar system. Clathrate hydrates probably formed in the early solar nebula, trapping volatile gases in icy solids that later aggregated, along with other primordial materials, into planets, moons, and other bodies. Clathrate hydrates could also be important on Mars, where the large relative abundance of carbon dioxide (CO_2) in the atmosphere, large deposits of subsurface ice, and very low surface temperatures could result in huge amounts of CO_2 clathrate on or near the surface. Such deposits may be responsible for the violent explosions of CO_2 gas and rapid water production that occur when Martian landslides suddenly
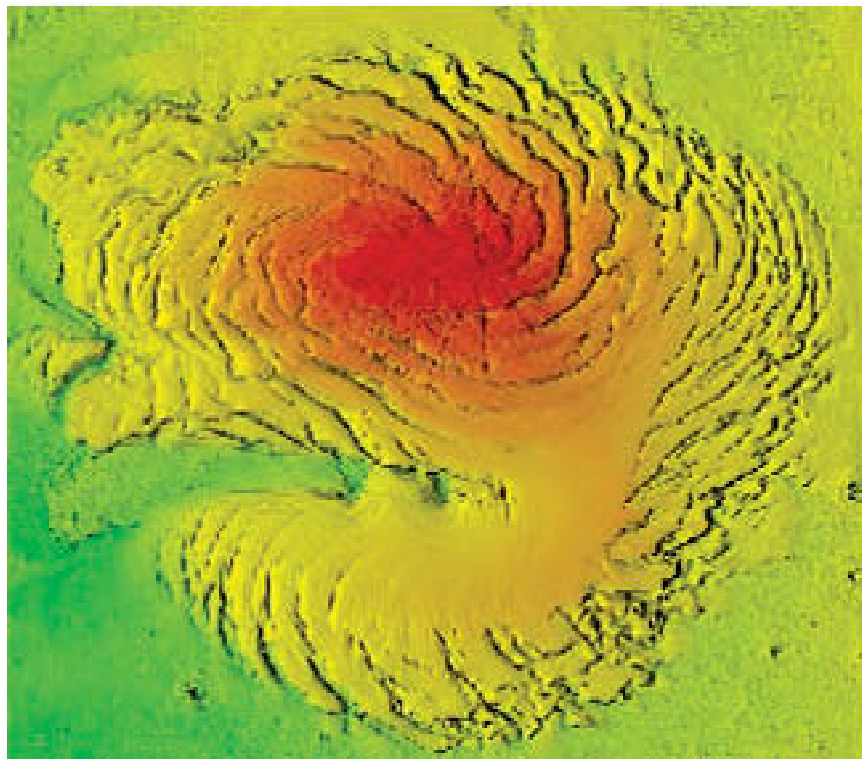

Small cage of hydrogen clathrate
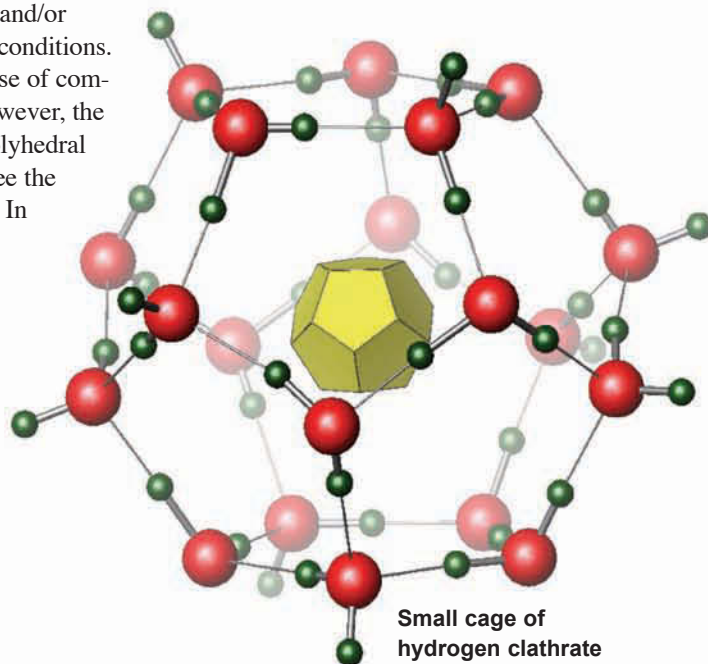
Figure 1. Possible Evidence for CO$_2$ Clathrates on Mars
Deposits of carbon dioxide clathrate could be responsible for the "volcanic" blowout shown in this photo of the north pole of Mars. This image was taken by the laser altimeter on the Mars Orbiter spacecraft. (Courtesy of Jon Pelletier, University of Arizona.)

release pressure, possibly leading to the "volcanic" blowouts and deep gully plows seen on the surface of Mars (Figure 1).

On Earth, clathrate hydrates containing mostly methane are found in ocean floor sediments and in permafrost. In fact, it is thought that clathrate hydrates contain the largest source of terrestrial hydrocarbons, which has sparked interest in methane clathrate hydrate, in particular, as a potential source of fossil fuel. Clathrate hydrates also play an unexpected role in the use of existing sources of fossil fuel. In arctic regions, hydrocarbon clathrates form in and can obstruct exploration wells and natural-gas pipelines—a serious problem for the petroleum industry.

Our recent neutron-diffraction studies at LANSCE suggest that hydrogen

clathrate could also play a role in our energy future. They show that hydrogen clathrate can reversibly store and release molecular hydrogen at a mass fraction of up to 3.77 percent at atmospheric pressure. This fraction is significantly higher than those possible with the magnesium nickel and lanthanum nickel hydrides, Mg_2NiH_4 (3.59%) and $LaNi_5H_6$ (1.37%), which are among the best available hydrogen-storage materials. Our studies also show that hydrogen clathrate can store significant quantities of molecular hydrogen in

as little as a few minutes or less and release it as fast or faster.

These properties could lead to a hydrogen storage system that could figure prominently in a hydrogen economy. But to develop such a system requires a detailed understanding of how hydrogen clathrate traps molecular hydrogen at various pressures and temperatures. Our neutron-diffraction studies have provided this information, whose main points are summarized in Figure 2.

Previous Studies of Hydrogen Clathrate

Hydrogen clathrate was discovered in 1999 by Yuri Dyadin's group during studies of mixtures of water and molecular hydrogen at various temperatures and pressures (Dyadin et al. 1999). These studies involved the use of differential thermal analysis, in which one measures the temperature of a sample that is evenly heated or cooled at a constant rate and plots this temperature as a function of time. Thus, differential thermal analysis allows measuring the heat capacity of a sample as a function of temperature, especially changes near phase transitions. Dyadin's group used this technique to detect the presence of hydrogen clathrate at 1000 to 4000 atmospheres and 0°C to 10°C.

Using x-ray and neutron diffraction, Mao's group showed (Mao et al. 2002) that this clathrate's framework structure is the so-called "cubic structure II," a face-centered-cubic structure.[1] The unit cell is made up of 8 large polyhedral cages (hexakaido-decahedra) and 16 small polyhedral

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[1] This description refers to the structure's symmetry and relates to a simple face-centered-cubic lattice as follows. For a simple lattice, if the origin of the unit cell's coordinate system is placed at a particular atom, the same type of atom will be seen in each corner of the unit cell and in the center of each face of the unit cell. For cubic structure II, the origin of the coordinate system is placed instead at the structure's center of inversion, which is at the center of a small cage.

cages (pentagonal dodecahedra), as shown in Figure 3. Known for more than 50 years, structure II is the framework structure of about one-half of all small-molecule hydrates known. In hydrogen clathrate, there are 136 water molecules in each unit cell, and each polyhedral cage has an oxygen atom at each vertex and a hydrogen atom on each edge.

Because they were unable to use their neutron-diffraction data to determine the numbers and positions of the hydrogen molecules in each type of cage, Mao's group used Raman spectroscopy to estimate the amount of hydrogen trapped in the clathrate and then inferred that the small and large cages hold up to two and four hydrogen molecules, respectively. However, with Raman spectroscopy, one cannot directly measure the amount and distribution of the hydrogen molecules in the clathrate.

Los Alamos Studies of Hydrogen Clathrate

In 2002, in collaboration with Mao's group, we began neutron diffraction studies of hydrogen clathrate, using LANSCE's High-Pressure Preferred-Orientation (HIPPO) diffractometer. For these studies, we built a special setup that allowed us to take advantage of the three-dimensional geometry of the diffractometer to obtain data of samples synthesized in situ under hydrostatic pressure over a range of temperatures (Figure 4). We made the pressure cell of aluminum alloy because aluminum is transparent to neutrons. The pressure cell can apply pressures between 1 and 7000 atmospheres and temperatures between 4 and 300 kelvins to a sample with a volume of up to 5 cubic centimeters.

The flux of thermal neutrons available at HIPPO, approximately 2.4×10^7 neutrons per centimeter squared
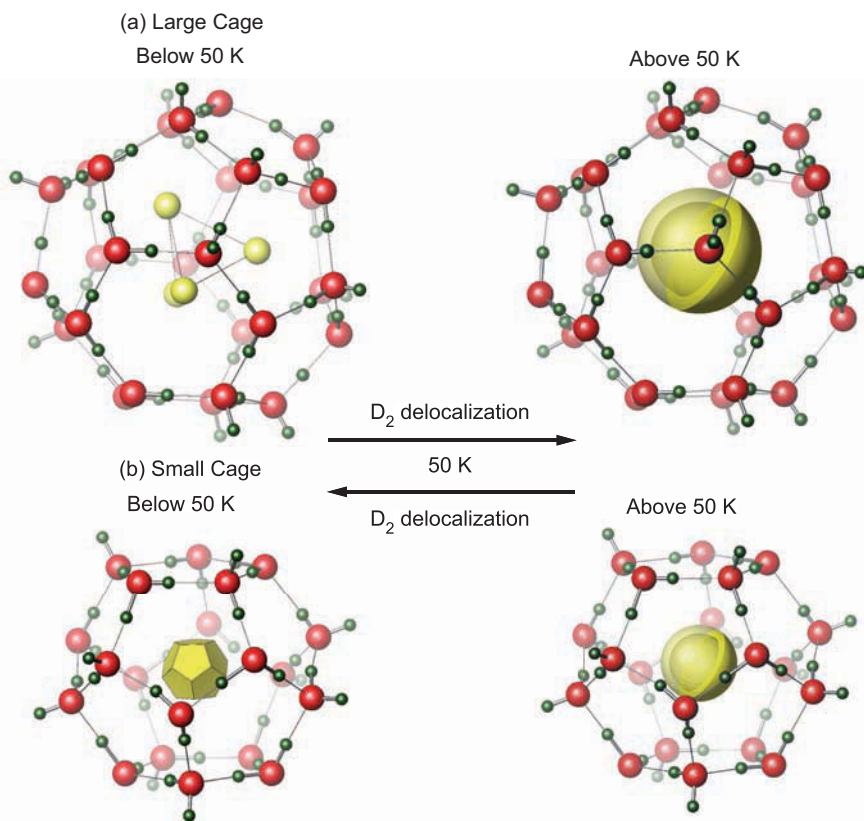

Figure 2. A Summary of Our Main Results
Two types of polyhedral cages are found in crystals of hydrogen clathrate. (Figure 3 shows how the cages are arranged in the clathrate's unit cell.) The red spheres are oxygen atoms in the hydrogen-bonded water molecules that form the cages. The small dark-green spheres are hydrogen atoms in the water molecules. The hydrogen molecules trapped inside the two types of cages are yellowish green. Our studies show that a large cage can hold up to four hydrogen molecules, and a small cage holds one hydrogen molecule. (a) Our studies also show that below 50 K, the four hydrogen molecules in a large cage form a stationary tetrahedral cluster with each hydrogen molecule pointing to the center of one of the cage's hexagonal faces. At higher temperatures, the tetrahedron rotates at the cage's center, the four hydrogen molecules are delocalized, and their density distribution is nearly spherically symmetrical. (b) Below 50 K, the hydrogen molecule in a small cage takes one of 20 orientations, describing a dodecahedron. At higher temperatures, the hydrogen molecule also rotates at the cage's center, and its density distribution also becomes nearly spherically symmetrical. (Reprinted with permission from K. A. Lokshin et al, *Phys. Rev. Lett.*, 93, p. 125503-2, 2004. Copyright 2004 by the American Physical Society.)

per second (n/cm²·s), is the highest in the world.[2] This flux, together with the diffractometer's high detection efficiency and the pressure cell's

comparatively large sample volume, allowed us to obtain high-quality neutron diffraction data in less than a minute—the shortest known time for a neutron diffraction measurement.

To further enhance the quality of the neutron diffraction data, we synthesized the clathrate using deuterated water (D_2O) instead of

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[2] Thermal neutrons are used for neutron diffraction studies of solids because the neutron wavelengths are comparable to interatomic spacings in crystalline materials.
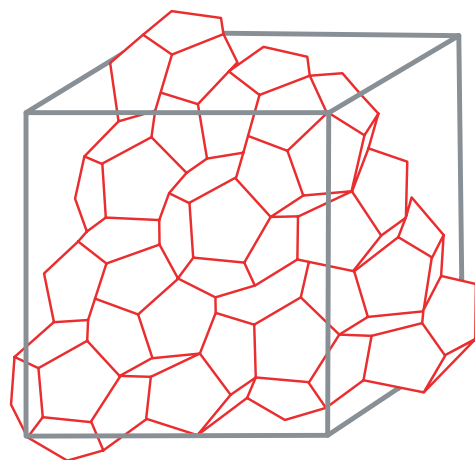
Figure 3. The Unit Cell of a Cubic Structure-II Clathrate
The unit cell consists of 136 water molecules, which form 16 small polyhedral cages (pentagonal dodecahedra) and 8 large polyhedral cages (hexakaidocahedra).
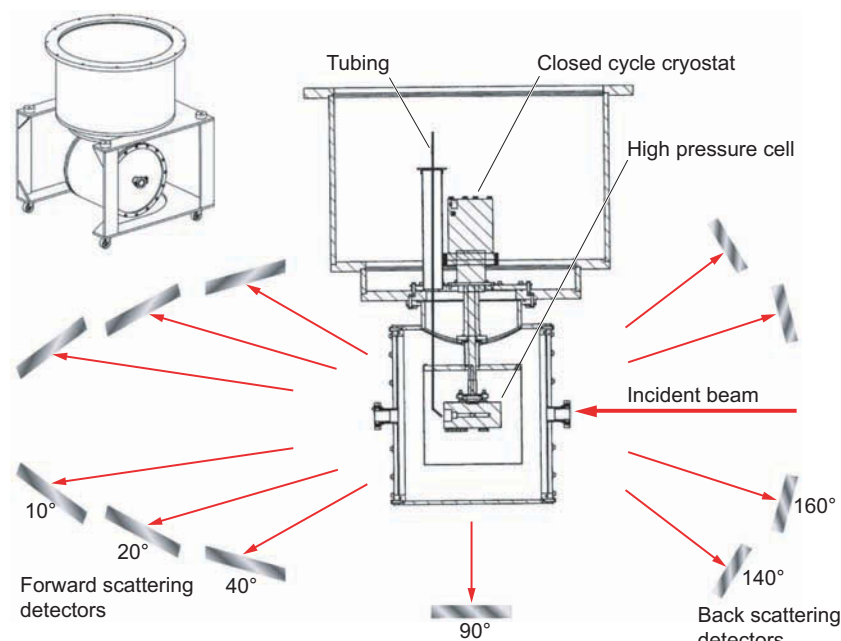

Figure 4. Hydrostatic Pressure Cell and Experimental Setup for Our Neutron-Diffraction Measurements
We synthesized deuterated samples of hydrogen clathrate inside the high-pressure cell and then measured the samples' crystal structures with neutron diffraction. The horizontal orientation of the cell and the complex detector geometry of the HIPPO diffractometer allowed fast collection of diffraction data from the sample without introducing scattering from impurities in the surroundings, which would degrade the quality of the data. (Reprinted with permission form *Rev. Sci. Instrum.*, **76**, p. 063909-2 (2005). Copyright 2005, American Institute of Physics.)

water (H_2O), and molecular deuterium (D_2) instead of molecular hydrogen (H_2). Replacing H_2 with D_2 improves the quality of neutron diffraction data by dramatically

decreasing the high background caused by the large incoherent scattering of neutrons by hydrogen atoms. Many studies have shown that substituting D for H in a com-

pound does not significantly affect its size or structure.[3]

To determine the numbers and positions of the hydrogen molecules, we applied a special addition to our "Rietveld refinement" of the data. Rietveld refinement analyzes the shapes and intensities of the Bragg peaks in x-ray or neutron diffraction data to provide information about structure, the average vibrational displacements of atoms from their lattice positions, and other phenomena. To use Rietveld refinement to locate deuterium molecules, we needed the neutron-scattering form factors for D_2. But at the time of our analysis, no one had calculated these form factors. To complete the analysis, we modeled D_2's form factors and used them in the Rietveld refinement assuming that the spatial distribution of D_2 in the cages was either localized (stationary) or spherically delocalized (rotating). It took us approximately one year to complete the refinement after collecting the data.

Details of the Trapped Deuterium Molecules

In the end, Rietveld refinement allowed us to extract, at a given pressure and temperature, the numbers and positions of the hydrogen molecules held in each type of cage (Lokshin et al. 2004). Figure 5 shows the number of deuterium molecules we measured in the large and small cages as a function of temperature for pressures of 1 and approximately 2000 atmospheres. (We use "bar" and "atmosphere" interchangeably since

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[3] However, an "isotope effect" is sometimes seen in the compound's physical or physiochemical properties, such as a clathrate's thermal-decomposition temperature. In fact, we measured a difference of about 5 to 10 kelvins at 1 atmosphere for the thermal-decomposition temperature of hydrogen clathrate made with H_2 compared with hydrogen clathrate made with D_2.
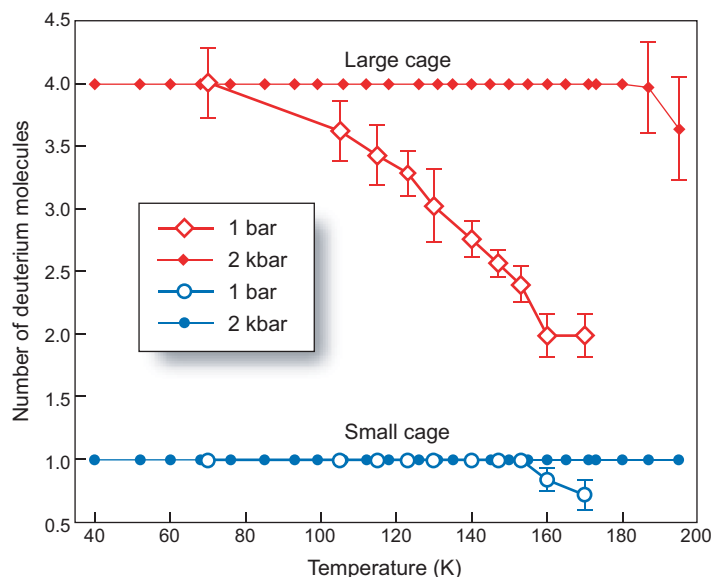
Figure 5. Number of Deuterium Molecules in Large and Small Cages
The large cages start losing deuterium molecules above 70 K at 1 atm and above
190 K at approximately 2000 atm. Similar behavior is observed for the small
cages. As the temperature increases, high pressure is required to stabilize the
clathrate for maximum deuterium-molecule occupancy. These data also show
that all the cages are filled with the maximum number of hydrogen molecules
for temperatures less than 70 K at 1 atm and less than 190 K at approximately
2000 atm. When all the cages are filled with the maximum number of hydrogen
molecules, the mass fraction of the stored hydrogen is 3.77%, rivaling the mass
fractions of the best hydrogen-storage materials. For reference, at 1 atm, liquid
nitrogen boils at 77 K, and dry ice evaporates at 195 K. (Reprinted with permission from
K. A. Lokshin et al, *Phys. Rev. Lett.*, 93, p. 125503-2, 2004. Copyright 2004 by the American Physical
Society.)

Figure 6. Spatial Distributions of Deuterium Molecules in Large Cages
These data are plotted as a function of temperature at 1 atm and approximately
2000 atm. (Reprinted with permission from K. A. Lokshin et al, *Phys. Rev. Lett.*, 93, p. 125503-3, 2004.
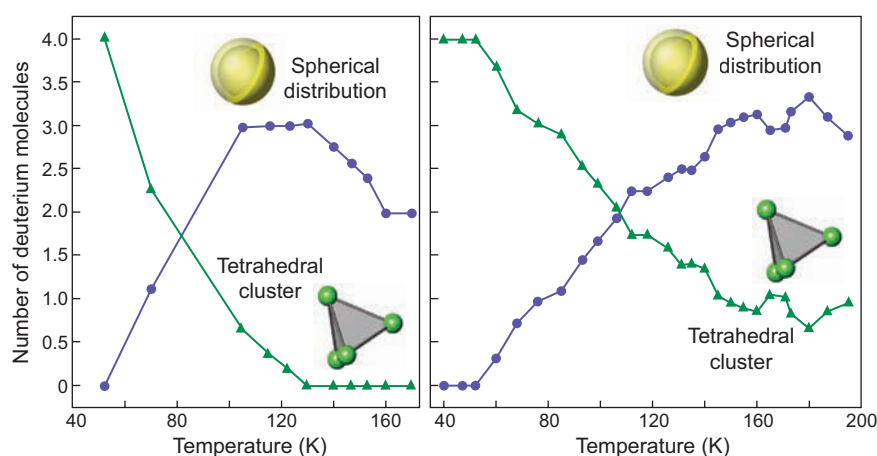Copyright 2004 by the American Physical Society.)

1 atmosphere equals 1.01325 bars.)
The large cage was found to hold 2 to
4 deuterium molecules, depending on
the pressure and temperature. At low
temperatures, a deuterium molecule is
located at each vertex of a tetrahedron
centered inside the cage. The deute-
rium molecules are 0.293 nanometer
from each other and 0.180 nanometer
from the center of the cage. Each deu-
terium molecule points toward a cen-
ter of one of the hexagons formed by
the oxygen atoms of the large cage.

For the small cage, we measured a
maximum occupancy number of only
one deuterium molecule. Rietveld
refinement determined that the neu-
tron scattering density of this mole-
cule is statistically distributed between
20 positions that point to the oxygen
atoms in the dodecahedral cage. For
both types of cages, Rietveld refine-
ment determined the distance between
the oxygen and deuterium molecules
to be 0.334 nanometer.

We also found that the hydrogen
molecules in both types of cages
become localized below 50 kelvins.
Below this temperature, the four
hydrogen molecules in a large cage
form a stationary tetrahedron, as
mentioned before. Above 50 kelvins,
the tetrahedron rotates at the cage's
center, so that the average spatial
distribution of the four hydrogen
molecules is nearly spherically sym-
metrical and the molecules are delo-
calized (Figures 2 and 6). A hydrogen
molecule trapped in a small cage
below 50 kelvins aligns along one of
20 directions. Above 50 kelvins, the
molecule rotates at the cage's center,
again leading to an average spatial
distribution that is nearly spherically
symmetrical.

Remarkably, the closest distance
between any two hydrogen molecules
in the tetrahedron is at least 30 per-
cent less than the closest distance
between any two hydrogen molecules
in solid hydrogen at 1 atmosphere.
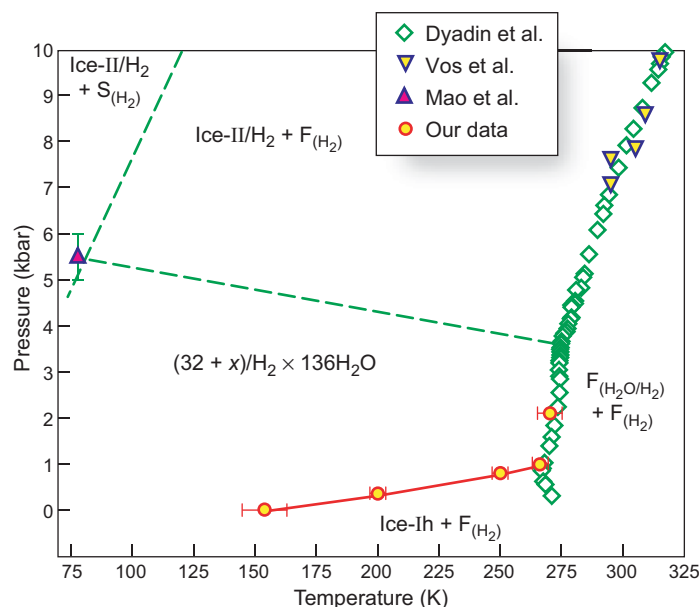This result tells us that the molecular

Figure 7. The Phase Diagram for Hydrogen Clathrate
This diagram includes experimental results from Yuri Dyadin's group, Mao's group, and the Los Alamos group. The region where the clathrate forms stably is bounded by the temperature and pressure axes, the nearly horizontal green dashed line, the line formed by the green diamonds (the melting curve), and the lower red solid line. All these results were obtained with mixtures that included an excess of hydrogen. "F" refers to fluid (water or liquid hydrogen). "S" refers to solid hydrogen. "$(32 + x)H_2 \times 136H_2O$" refers to the 136 water molecules in a unit cell of hydrogen clathrate, plus the $32 + x$ hydrogen molecules trapped in cages, where x varies from 0 to 16.

framework surrounding the hydrogen molecules affects the local density of the molecules. It also suggests that it may be possible to store molecular hydrogen at higher densities by using an appropriate framework, not necessarily the framework provided by a clathrate's cages.

The Phase Diagram for Hydrogen Clathrate

Figure 7 is the hydrogen–water phase diagram. This plot shows all the pressure–temperature regions and their boundaries where water and hydrogen molecules form stable crystalline phases. Figure 7 combines our experimental data with the data of the Dyadin and Mao groups that pertain

to the phase transitions of hydrogen clathrate. All measurements were made with mixtures that included an excess of hydrogen.

The stable-clathrate region is bounded by the temperature and pressure axes and three experimentally determined curves. Within the stable-clathrate region, no ice phases are present—only clathrate and excess hydrogen. The three bounding curves are the following: (1) The melting curve (the line formed by the green diamond symbols) is where the clathrate [labeled "$(32 + x)H_2 \times 136H_2O$"] is in equilibrium with a water solution of gaseous hydrogen [denoted as "$F_{(H_2O/H_2)}$," where F stands for fluid]. (2) The high-pressure boundary line (the lower, dashed green line) is where the clathrate is in equilibrium

with a solution of gaseous hydrogen in ice-II (labeled "ice-II/H_2"). The ice-II/H_2 phase was found to be stable from 7 to 20 kilobars. (3) The low-pressure boundary line (solid red line) is where the clathrate is in equilibrium with ice-Ih. Several points on this line are from our measured data: 163 kelvins at 1 bar, 200 kelvins at 0.35 kilobar, and 265 kelvins at 1.0 kilobar.

Fast Synthesis

We made our first neutron-diffraction measurements of the hydrate with starting mixtures of liquid D_2O and gaseous D_2. In those experiments, the clathrate formed very slowly. (Sometimes, water did not fully convert to the clathrate after several days.) We initially attributed this effect to the small surface area of the liquid D_2O exposed to the gaseous D_2 and decided to increase the surface area by starting with a mixture of gaseous D_2 and powdered ice instead of water. The particles in the powdered ice had diameters of about 500 micrometers. To our surprise, the clathrate formed extremely quickly with powdered ice (Figure 8)—a result of extreme importance for developing a viable hydrogen-storage system. [This hydrogen storage (release) method could involve, for example, going from lower (higher) pressure to higher (lower) pressure at a constant temperature across the red line shown in Figure 7.]

We also prepared hydrogen clathrate from a chunk of ice-Ih with a mass of about 1 gram and a volume comparable to the volume of water used for clathrate synthesis. The diffraction patterns taken during the synthesis of hydrogen clathrate at 250 kelvins and 1.5 kilobars are shown in Figures 8(d)–(f). The formation of clathrate from the chunk of ice was complete in about 1.5 to 2 hours, which is slower than the synthesis from powdered ice but at least 100 times faster than the synthesis
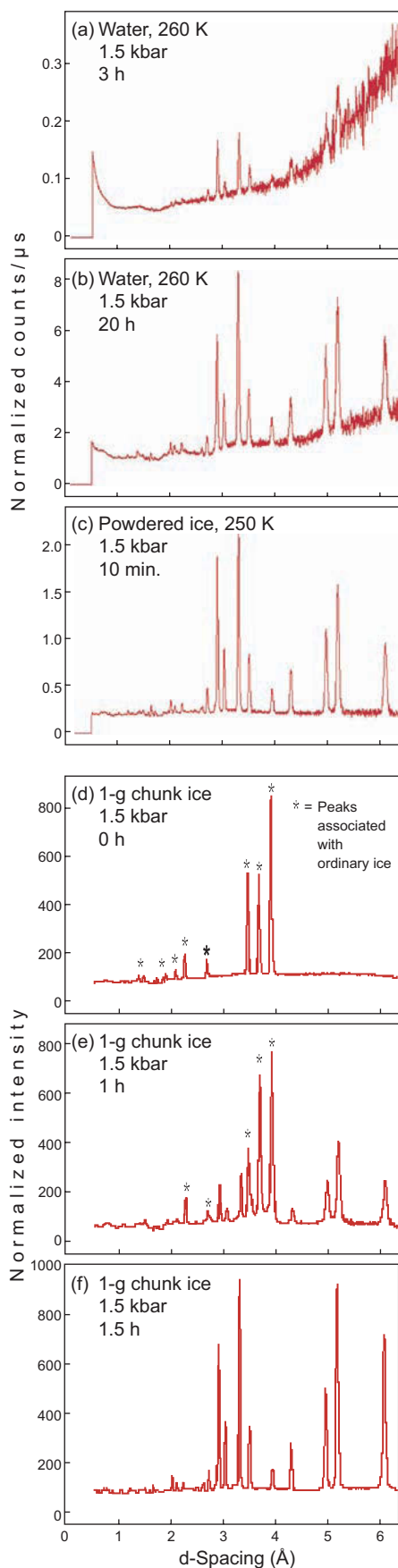
Figure 8. Neutron Diffraction Data for Hydrogen Clathrate Formed in Different Ways
A comparison of plots (a) and (b) with plot (c) reveals that hydrogen clathrate forms more slowly from water than from powdered ice. It also forms somewhat slowly from chunk ice, as shown in (d) through (f). The asterisks denote peaks associated with ordinary ice. When all these peaks disappear, the sample is 100% hydrogen clathrate.

from water. We also found that fast clathrate formation did not occur when we used (bulk) amorphous ice—prepared by chilling water at a pressure of 2.2 kilobars—as the starting material.

Thus, the fast synthesis of hydrogen clathrate from ice cannot be explained only by the difference between the reaction surface areas of powdered ice and water. We believe fast synthesis could occur because ice-Ih is more porous than water. In fact, ice-Ih is much less dense (9 percent less) than water because ice-Ih contains many small cavities. These cavities could be large enough for hydrogen molecules to enter under pressure. We believe that the penetration of the cavities by molecular hydrogen promotes the conversion of ice-Ih to clathrate hydrate.

Conclusions

Until recently, hydrogen clathrate did not appear to have much practical value. It was hard to make, and some of its most important properties were unknown. The clathrate could be synthesized only at pressures of many thousands of atmospheres and/or low temperatures, and it could take several days or more to complete the synthesis. In addition, the precise amounts of molecular hydrogen that could be stored in the material at various pressures and temperatures were unknown.

However, our recent neutron-diffraction studies show that hydrogen clathrate has the potential for use as a practical hydrogen-storage medium. Our studies show that the hydrate can be synthesized in a few minutes from ordinary powdered ice. And when synthesized at 1 atmosphere and liquid-nitrogen temperatures, the clathrate has an H_2 mass fraction of 3.77 percent, rivaling the mass fractions of the best hydrogen-storage materials. Most important, we have measured the numbers and positions of the hydrogen molecules stored in both types of the clathrate's molecular cages at various pressures and temperatures. This information is essential for benchmarking future studies of this and related clathrates and could be used to develop hydrogen storage systems with significant potential for enabling a hydrogen economy. ■

Further Reading

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